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## Assessing Selenium Contamination in the Irrigated Stream-Aquifer System of the Arkansas River, Colorado

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**Abstract:** Prudent interventions for reducing selenium (Se) in groundwater and streams within an irrigated river valley must be guided by a sound understanding of current field conditions. An emerging picture of the nature of Se contamination within the Lower Arkansas River Valley in Colorado is provided by data from a large number of groundwater and surface water sampling locations within two study regions along the river. Measurements show that dissolved Se concentrations in the river are about double the current Colorado Department of Public Health and Environment (CDPHE) chronic standard of  $4.6 \mu\text{g L}^{-1}$  for aquatic habitat in the upstream region and exceed the standard by a factor of 2 to 4 in the downstream region. Groundwater concentrations average about  $57.7 \mu\text{g L}^{-1}$  upstream and  $33.0 \mu\text{g L}^{-1}$  downstream, indicating a large subsurface source for irrigation-induced dissolution and mobilization of Se loads to the river and its tributaries. Inverse correlation was found between Se concentration and the distance to the closest identified shale in the direction upstream along the principal groundwater flow gradient. The data also exhibited, among other relationships, a moderate to strong correlation between dissolved Se and total dissolved solids in groundwater and surface water, a strong correlation with uranium in groundwater, and power relationships with nitrate in groundwater. The relationship to nitrate, derived primarily from N fertilizers, reveals the degree to which dissolved Se depends on oxidation and inhibited reduction due to denitrification and suggests that there are prospects for reducing dissolved Se through nitrate control. Current and future results from these ongoing studies will help provide a foundation for modeling and for the discovery of best management practices (BMPs) in irrigated agriculture that can diminish Se contamination. [PUBLICATION ABSTRACT]

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### Full text: Headnote

Prudent interventions for reducing selenium (Se) in groundwater and streams within an irrigated river valley must be guided by a sound understanding of current field conditions. An emerging picture of the nature of Se contamination within the Lower Arkansas River Valley in Colorado is provided by data from a large number of groundwater and surface water sampling locations within two study regions along the river. Measurements show that dissolved Se concentrations in the river are about double the current Colorado Department of Public Health and Environment (CDPHE) chronic standard of  $4.6 \mu\text{g L}^{-1}$  for aquatic habitat in the upstream region and exceed the standard by a factor of 2 to 4 in the downstream region. Groundwater concentrations average about  $57.7 \mu\text{g L}^{-1}$  upstream and  $33.0 \mu\text{g L}^{-1}$  downstream, indicating a large subsurface source for irrigation-induced dissolution and mobilization of Se loads to the river and its tributaries. Inverse correlation was found between Se concentration and the distance to the closest identified shale in the direction upstream along the principal groundwater flow gradient. The data also exhibited, among other relationships, a moderate to strong correlation between dissolved Se and total dissolved solids in groundwater and surface water, a strong correlation with uranium in groundwater, and power relationships with nitrate in groundwater. The relationship to nitrate, derived primarily from N fertilizers, reveals the degree to which dissolved Se depends on oxidation and inhibited reduction due to denitrification and suggests that there are prospects for reducing dissolved Se through nitrate control. Current and future results from these ongoing studies will help provide a foundation for modeling and for the discovery of best management practices (BMPs) in irrigated

agriculture that can diminish Se contamination.

Abbreviations: BMP, best management practices; CDPHE, Colorado Department of Public Health and Environment; DO, dissolved oxygen; LARV, Lower Arkansas River Valley; ORP, oxidation reduction potential; TMDL, total maximum daily load.

Over the last two to three decades, the presence of high concentrations of Se in surface and groundwaters has emerged as an issue of serious concern in the western United States (Engberg and Sylvester, 1993), northern Europe (Alfthan et al., 1994; Bye and Lund, 1982), and Asia (Afzal et al., 2000; Mizutani et al., 2001; Zhang et al., 2008). Problem sites in the western United States include California (Tracy et al., 1990; Nolan and Clark, 1997) and western Colorado in the lower Gunnison River Basin (Butler and Leib, 2002), with high concentrations found particularly in intensively irrigated alluvial valleys with Se-bearing geologic formations (Nolan and Clark, 1997), where the processes of Se dissolution, transport, and bioaccumulation can be accelerated. Intensive irrigation of alluvial soils, derived from and interspersed with weathered marine sedimentary rock layers, coupled with nitrification of N fertilizers, can impel salts and other minerals, such as Se, through the underlying alluvial aquifer in flows that eventually make their way to the river and its tributaries. In addition, irrigation of crops increases the consumptive use of water in the watershed, leading to evaporative concentration of salts and other minerals. Likely, the most famous incidence of Se poisoning due to high concentrations induced by irrigation occurred at Kesterson National Wildlife Refuge in the western San Joaquin Valley in California. Bioaccumulation of Se occurred because of high concentrations in subsurface agricultural drainage water from irrigated fields that was carried to Kesterson by the San Luis Drain (Ohlendorf and Santolo, 1994). Hundreds of deaths and deformities to fish and waterfowl occurred due to toxic levels of Se within the drain, reservoir, and groundwater. Since this disaster, preliminary studies have been conducted in other regions threatened by Se contamination caused by irrigation drainage (National Research Council, 1989; Seiler et al., 1999, 2003). One of these regions is the Lower Arkansas River Valley (LARV) in southeastern Colorado. Intensively irrigated for more than 100 yr, the LARV has served as one of Colorado's most productive agricultural areas. The valley now faces the challenge of improving water management to recover productivity that has been diminished due to salinization and waterlogging, to salvage water lost to nonbeneficial consumptive use, and to lessen nonpoint source loading of salts and Se to the river, menaces that are derived from overirrigation, canal seepage, and poor drainage (Burkhalter and Gates, 2005, 2006; Gates et al., 2006; Mueller Price and Gates, 2008). Limited studies by Ortiz et al. (1998), Seiler et al. (2003), and Divine and Gates (2006) have indicated river dissolved Se concentrations that exceed the current CDPHE and U. S. Environmental Protection Agency (USEPA) chronic criterion for aquatic habitat protection ( $4.6 \mu\text{g L}^{-1}$ ; defined as the 85th percentile of an acceptable sample set). Having designated all segments of the Lower Arkansas River as impaired for Se, the CDPHE commissioned the study reported herein to more accurately characterize the nature and extent of the Se contamination problem in the groundwater and surface water of the irrigated stream-aquifer system.

All segments of the LARV, extending from Pueblo, CO to the Colorado-Kansas state line and covering about 186,000 ha, were placed in 2004 on the Clean Water Act section 303(d) list for Se impairment and remain on the current list, joining 44 other stream segments in five of the seven major watersheds in Colorado. These river segments represent similar stretches of irrigation-affected streams in the western United States for which plans will be needed for mitigating the impacts of nonpoint source Se loading to streams. In response to the directives of the Clean Water Act, the Colorado Water Quality Control Division of the CDPHE currently is assessing both point and nonpoint sources of Se along impaired segments of the LARV to determine total maximum daily loads (TMDLs) from these sources that will bring concentrations along the segments into compliance with the Se standard. This poses a formidable problem: the need to develop TMDLs and to implement associated BMPs over broad and variable regions of irrigated landscape. The challenge is to figure out how to alter water management and cultivation practices to meet regulatory and performance goals for the ecological health of the

river system, while doing so in a way that preserves productive irrigated agriculture.

A trace element that widely occurs in nature, Se varies greatly in its distribution among different geologic formations. Its accumulation as a solute in the natural environment, with consequential adverse impacts, is affected by several hydrochemical processes. When anthropogenic processes related to intensive irrigated agriculture are superimposed, additional complicating features emerge. The relationships inherent to these interacting processes are fairly well understood from laboratory analysis but until recently have yet to be quantified in extensive spatiotemporal field measurements. Enhanced understanding of these relationships is especially important when trying to find ways to broadly decrease Se concentrations in the field.

Shales, including those of the Cretaceous period, are geologic materials that are known to contain high Se concentration. In the Arkansas River Basin Cretaceous shale [Pierre Shale, Carlisle Shale, Graneros Shale, and Smoky Hill Shale formations (the last three have been identified in the study regions reported in this paper)] has been found underlying and interspersed in a weathered form within the Arkansas River alluvium (Scott, 1968; Sharps, 1976; Scott et al., 1978). Cretaceous shales also include black shales (containing concentrations of about  $600 \text{ mg kg}^{-1}$ ), phosphate rocks ( $1\text{--}300 \text{ mg kg}^{-1}$ ), and other formations that potentially give rise to seleniferous soils (Rosenfield and Beath, 1964). Selenium exists in shale in the form of seleno-pyrite, or iron diselenide ( $\text{FeSe}_2$ ). Bye and Lund (1982) reported Se concentrations in pyrite as 10 to  $100 \text{ mg kg}^{-1}$ . Pyrite analyzed in Japan (Mizutani et al., 2001) yielded a Se concentration of 5.6 to  $300 \text{ mg kg}^{-1}$ . Soils originating from cretaceous shale, such as those found in Colorado and other western states, tend to have high ( $2\text{--}10 \text{ mg kg}^{-1}$ ) Se concentrations whereas the Northwest, Southeast, and Great Lake states have soil concentrations below  $0.05 \text{ mg kg}^{-1}$  (Kubota et al., 1967; Martens and Suarez, 1997).

The dissolution of Se from geologic and soil materials and its transformation from one species to another is substantially influenced by reduction-oxidation (redox) reactions. Selenium can exist in four principal forms, each with a different oxidation state: selenate ( $\text{SeO}_4^{2-}$ )(+6), selenite ( $\text{SeO}_3^{2-}$ )(+4), elemental  $\text{Se}(0)$ , and selenide( $-2$ ). Redox reactions, inherently slow, are catalyzed by bacteria, which use them in respiration processes (Macy et al., 1989; Oremland et al., 1990). Bacterial respiration transfers electrons from an energy source (e.g., organic matter, or minerals such as  $\text{FeS}_2$  or  $\text{FeSe}_2$ ), termed electron donors, to oxygenated species [dissolved oxygen ( $\text{DO}$ ), nitrate ( $\text{NO}_3^-$ ),  $\text{SeO}_4^{2-}$ ], termed electron acceptors. The following conditions are needed for redox reactions to occur (Korom, 1992): bacteria capable of reducing oxygenated species, electron donors serving as the food source of bacteria, and electron acceptors.

The dissolution of sulfide from pyrite ( $\text{FeS}_2$ ) and the mobilization of  $\text{SO}_4^{2-}$  as a result of oxidation by  $\text{NO}_3^-$  have been well documented (Frind et al., 1990; Postma et al., 1991; Grimaldi et al., 2004). In this redox reaction,  $\text{FeS}_2$ , which is oxidized to liberate  $\text{SO}_4^{2-}$ , is the electron donor and  $\text{NO}_3^-$ , which is reduced to  $\text{N}_2$ , is the electron acceptor. Due to similarities in the electron valence structure of S and Se, a similar redox reaction occurs in the case of  $\text{FeSe}_2$ . In this process,  $\text{SeO}_4^{2-}$  is mobilized and introduced into the groundwater system, and is transported according to the chemical conditions of the aquifer in subsurface flows that feed surface streams and lakes. Once it enters an aquatic environment, Se can rapidly bioaccumulate through the food chain and attain toxic concentrations. The extent and severity of the contamination of aquatic habitats by Se has been documented and discussed by Lemly (1999, 2004) and McIntyre et al. (2008).

In 2003, Colorado State University initiated a regional-scale (order of  $10^4 \text{ ha}$ ) study of Se contamination in the irrigated stream-aquifer system of the LARV. The research includes extensive monitoring of Se concentrations in the shallow unconfined alluvial aquifer, in tributaries and drains, and in the main stem of the Arkansas River within two study regions covering 50,600 ha and 55,200 ha, respectively. Objectives of this initial phase of a multi-year effort are (i) to characterize the nature, severity, and the spatiotemporal variability of Se concentrations and loads in groundwater and surface waters; (ii) to examine relationships between Se concentration and other hydrogeochemical properties and processes; (iii) to search for correspondence with

maps and other indicators of geological formations that underlie irrigated ground, and finally; (iv) to help build a database needed to support eventual computational modeling of Se mobilization, transport, and transformation under current conditions and under alternative improved irrigation and river management strategies.

This paper presents some of the major findings of this effort, believed to constitute one of the most extensive programs ever attempted for monitoring dissolved Se in a field setting within an irrigated river valley. It explores how the processes that affect Se in the natural environment display themselves over regional scales within a stream-aquifer system that is affected both by natural conditions and by intensive irrigated agriculture. A special focus of this paper is on indicators of the impact of redox reactions on the incidence and pattern of dissolved Se. Insights gained should prove useful not only to the future enhancement of the Arkansas River but to the understanding of Se occurrence and management in similar settings throughout the western United States and abroad.

## Materials and Methods

### Study Sites

The occurrence and concentration of dissolved Se were examined in two representative study regions along the LARV in Colorado. The first study region, referred to as the upstream study region, is located upstream of John Martin Reservoir and extends between just west of the town of Manzanola to near Las Animas. This region encompasses a total of about 50,600 ha (125,000 acres), of which about 26,400 ha (65,300 acres) are irrigated from canals or pumping wells. Samples routinely were taken from 45 groundwater observation wells, four locations in tributaries and drains, and 10 locations along the river (Fig. 1). Samples also were taken from an additional 61 observation wells on an aperiodic schedule for use in expanding the dataset for further exploration of relationships among variables. Currently six sampling events have been undertaken and analyzed for this region-June 2006, May 2007, October 2007, March 2008, June 2008, and August 2008-and are reported herein.

The second, and more extensively-studied region, is located downstream of John Martin Reservoir and stretches between the city of Lamar eastward to the Colorado-Kansas state line. This downstream study region is located approximately 30 km east of the eastern edge of the upstream study region and covers a total of about 55,200 ha (136,300 acres), of which about 33,000 ha (81,600 acres) are irrigated from canals that divert water from the river or from alluvial pumping wells. A total of 47 groundwater observation wells, 12 locations in tributaries and drains, and six locations along the river have been routinely monitored for Se and related constituents (Fig. 1). An additional 59 observation wells were sampled aperiodically. Methods and results of 33 sampling events over the period April 2003 through July 2008 are reported herein.

### Groundwater Monitoring

Groundwater samples were gathered from observation wells cased with slotted 0.064-m (2.5-in) diam. PVC that intercepted relatively shallow water tables. The water level in each well was read with an electronic water level meter and recorded just before purging the well. For the upstream samples, the water table depth from ground surface at the time of sampling varied between 0.3 and 10.8 m, averaging 3.0 m. Downstream, the water table depth ranged from 0.4 to 9.8 m, averaging 3.9 m.

A low-flow QED Sample Pro (QED Environmental Systems, Ann Arbor, MI) bladder pump and decontaminated dual 0.0064-m (0.25-in.) diam. polyethylene tube were used to extract flow from each well. The well was purged at the beginning of each sampling event using an initial pumping rate of 0.20 to 0.30 L min<sup>-1</sup>. An electronic drawdown indicator was set at approximately 0.30 m below the static water level in the well. If the drawdown in the well was greater than about 0.30 m, the indicator triggered an automatic shut-off in the pump. If the well was not able to recharge at these pumping rates, purging was reduced to the minimum flow rate specific to the pump.

During purging, indicator properties of pH, EC, temperature, dissolved oxygen (DO), and oxidation reduction potential (ORP) were measured at time intervals of approximately 3 min using a flow-through cell and a YSI

600QS Multiparameter Sampling System (YSI, Inc., Yellow Springs, OH), routinely calibrated with standard solutions. The extracted well water was considered representative of the surrounding groundwater when four indicator properties had stabilized for two consecutive readings as follows:  $\pm 0.1$  for pH,  $\pm 3\%$  for EC,  $\pm 10\%$  for DO, and  $\pm 10$  mV for ORP. Sampling began when the indicator properties had stabilized, or after three well volumes had been purged from the monitoring well.

Samples for total dissolved Se concentration,  $C^{sub} Se^{\wedge}$ , dissolved uranium concentration,  $C^{sub} U^{\wedge}$ , and specific salt ion concentrations were collected at a flow rate of approximately 0.10 to 0.20 L per minute. Additionally, the  $C^{sub} Se^{\wedge}$ ,  $C^{sub} U^{\wedge}$ , and salt ion samples were filtered through disposable in-line 0.003  $m^{sup} 2^{\wedge} 0.45 \mu m$  capsule filters.  $C^{sub} Se^{\wedge}$  samples were taken in a clean 0.12 L plastic (polypropylene or polyethylene) bottle, while  $C^{sub} U^{\wedge}$  and salt ion samples were taken in clean 0.25 L plastic bottles. Samples for  $C^{sub} Se^{\wedge}$  and  $C^{sub} U^{\wedge}$  were preserved at pH  $< 2$  by adding about 0.005 L of a 10% solution of ultra-pure nitric acid in reagent water per liter of sample (approximately 0.00625 L per 0.12-L sample bottle) before sample collection. All samples were stored on ice (at about 4°C).

#### Surface Water Monitoring

Surface water samples were collected in the river, tributaries, and drains using a peristaltic pump. Samples for  $C^{sub} Se^{\wedge}$  and  $C^{sub} U^{\wedge}$  were filtered through disposable in-line 0.003 or 0.006  $m^{sup} 2^{\wedge} 0.45 \mu m$  capsule filters and placed in clean 0.12 L plastic bottles, appropriate for storing dissolved minerals. Samples typically were taken from a stream at about mid-flow depth at about the center of the cross-section (i.e., at midway along the top width). In situ measurements of pH, temperature, EC, DO, and ORP were made just before sample collection using a decontaminated and calibrated YSI 600QS Multiparameter Sampling System. As with the groundwater samples, surface water samples were acidified and stored on ice.

Surface water samples from the river, tributaries, and drains were collected over a wide range of flow rates. However, the flow rates during 2003 to 2005 tended to be quite low due to drought conditions in the LARV (Gates et al., 2006; Mueller Price and Gates, 2008).

#### Blank and Duplicate Samples

Field blanks for groundwater and surface water were taken once per day before sample collection to ensure that sample contamination had not occurred in the field. Field blanks were generated by processing distilled/deionized water through each of the sample steps and field equipment (i.e., tubing, pump, and filters for groundwater samples). Analysis of field blanks in the laboratory confirmed that equipment had not been contaminated.

Field duplicates for groundwater and surface water also were gathered to assess the precision of the field sampling and analytical processes. At least one field duplicate was taken every day, collected in rapid succession to the primary sample. A total of 206 field duplicates of groundwater samples and 60 duplicates of surface water samples were gathered and analyzed. Average difference between original and duplicate samples was below 4% for groundwater and 2% for surface water.

#### Laboratory and Data Analysis

Groundwater and surface water samples were analyzed for  $C^{sub} Se^{\wedge}$  at the Olson Biochemistry Laboratories at South Dakota State University in Brookings, SD (USEPA certified) using Official Methods of Analysis of AOAC International, 17th edition, test number 996.16 Selenium in Feeds and Premixes, Fluorometric Method. This method is used to determine the concentration of  $SeO^{sub} 3^{\wedge}$  in the sample from the field. Total recoverable Se ( $C^{sub} Se^{\wedge}$ ) then is determined by reducing all forms of Se within the field sample to  $SeO^{sub} 3^{\wedge}$  using hydrochloric acid and reconducting the fluorometric analysis. The concentration of  $SeO^{sub} 4^{\wedge}$  is then estimated by subtracting the concentration of  $SeO^{sub} 3^{\wedge}$  determined before adding HCL from the concentration determined after adding HCL. Although developed specifically for testing animal feeds, the fluorometric method provides repeatable analysis for  $C^{sub} Se^{\wedge}$  near criterion levels with an estimated coefficient of variation (CV) of 4 to 5%. Double tests were completed on each water sample and the average

was reported. The detection limit was  $0.4 \mu\text{g L}^{-1}$ .

Severn Trent Laboratories, Inc. in Earth City, MO (certified under the National Environmental Laboratory Accreditation Program) analyzed groundwater and surface water samples for  $\text{C}^{\text{sub}} \text{U}^{\text{A}}$  using inductively coupled plasma-mass spectrometry. The protocol followed in the analysis was method 200.8 in USEPA (1994). The detection limit was  $1.0 \mu\text{g L}^{-1}$ .

Samples gathered for analysis of specific salt ion concentrations were analyzed by Ward Laboratories, Inc. in Kearney, NE using standard methods. Ward Laboratories, Inc. participates in the check sample program with the North American Proficiency Testing Program. Samples were analyzed for concentration of sodium,  $\text{C}^{\text{sub}} \text{Na}^{\text{A}}$  (USEPA 1983, Method 273.1); calcium,  $\text{C}^{\text{sub}} \text{Ca}^{\text{A}}$  (USEPA 1983, Method 215.1); magnesium,  $\text{C}^{\text{sub}} \text{Mg}^{\text{A}}$  (USEPA 1983, Method 242.1); potassium,  $\text{C}^{\text{sub}} \text{K}^{\text{A}}$  (USEPA 1983, Method 258.1); nitrate,  $\text{C}^{\text{sub}} \text{NO}^{\text{sub}} 3^{\text{A}}$  (USEPA 1983, Method 353.2); sulfate,  $\text{C}^{\text{sub}} \text{SO}^{\text{sub}} 4^{\text{A}}$  (USEPA 1983, Method 375.4); chloride,  $\text{C}^{\text{sub}} \text{Cl}^{\text{A}}$  (USEPA 1983, Method 325.1); carbonate,  $\text{C}^{\text{sub}} \text{CO}^{\text{sub}} 3^{\text{A}}$  (APHA 1992, Method 2320-B); bicarbonate,  $\text{C}^{\text{sub}} \text{HCO}^{\text{sub}} 3^{\text{A}}$  (APHA 1992, Method 2320-B); and boron,  $\text{C}^{\text{sub}} \text{B}^{\text{A}}$  (APHA 1992, Method 4500-B-D). Statistical analysis of laboratory and field data was conducted using @RISK (version 4.5) (Palisade Corporation, 2005) and Statistica (version 8.0) (Statsoft, Inc., 2008) software. This included summary statistics, correlation, nonlinear regression, and fitting of probability distributions. Outlier analysis was performed on all data sets using Chauvenet's criterion (Taylor, 1997).

## Results and Discussion

### Severity and Variability of Selenium Concentrations

Tables 1 and 2 summarize the basic statistical characteristics for  $\text{C}^{\text{sub}} \text{Se}^{\text{A}}$ ,  $\text{C}^{\text{sub}} \text{U}^{\text{A}}$ , salt ions, and other properties in all routinely monitored groundwater and river water samples, respectively, collected over all sample periods within the upstream and downstream regions. A similar summary is given in Table 3 for samples taken from tributaries and drains in the two regions.

A subset of the samples was analyzed to determine the fraction of dissolved Se in the form of  $\text{SeO}^{\text{sub}} 4^{\text{A}}$ . Analysis of 116 groundwater samples in the upstream study region and 42 groundwater samples in the downstream study region revealed that on average about 91 and 92%, respectively, of the dissolved Se indicated by reported  $\text{C}^{\text{sub}} \text{Se}^{\text{A}}$  values was in the form of  $\text{SeO}^{\text{sub}} 4^{\text{A}}$ . A subset of 16 surface water samples from the downstream region indicated that an average of about 81% of dissolved Se was in the form of  $\text{SeO}^{\text{sub}} 4^{\text{A}}$ .

Over all of the gathered groundwater samples, values as high as 1360 and 3760  $\mu\text{g L}^{-1}$  were detected in the upstream and downstream regions, respectively. The statistical mean value of  $\text{C}^{\text{sub}} \text{Se}^{\text{A}}$  measured in routinely-monitored groundwater in the upstream study region was 57.7 and was 33.0  $\mu\text{g L}^{-1}$  downstream, both markedly larger than the current CDPHE standard of 20  $\mu\text{g L}^{-1}$  established for protection of drinking water for livestock. Moreover, concentrations this high, 7 to 13 times the stream chronic standard, in groundwater return flows pose challenges to the health of the stream system.

The data reveal substantial spatial and temporal variability in  $\text{C}^{\text{sub}} \text{Se}^{\text{A}}$  in groundwater. Additional details are provided in Donnelly (2005). Figure 2 provides examples of spatial contours of measured groundwater  $\text{C}^{\text{sub}} \text{Se}^{\text{A}}$  for representative sample periods for the upstream and downstream regions. The variation in spatial statistics in groundwater  $\text{C}^{\text{sub}} \text{Se}^{\text{A}}$  over time is illustrated by the box-and-whisker plots for the routinely-sampled observation wells in the downstream region in Fig. 3. Spatial CV values for  $\text{C}^{\text{sub}} \text{Se}^{\text{A}}$  across the routinely-sampled wells varied from 108 to 185% over the sample periods in the downstream region and from 139 to 339% over the sample periods in the upstream region. This substantial variability is due in part to differences in natural hydrologic processes and irrigation water application over the regions and over time, the variety of geologic and soil conditions with their associated physical and chemical properties, and an array of other characteristics within the stream-aquifer system, including redox conditions as discussed below.

Mean values of measured  $\text{C}^{\text{sub}} \text{Se}^{\text{A}}$  in tributaries and drains in the upstream and downstream regions were



about 13.1 and 15.8  $\mu\text{g L}^{-1}$ , respectively. The total of 57 samples taken from the 10 sampling locations in the Arkansas River in the upstream study region had a mean value of 7.0  $\mu\text{g L}^{-1}$ . The 85th percentile value was 10.2  $\mu\text{g L}^{-1}$ , exceeding the current CDPHE chronic standard of 4.6  $\mu\text{g L}^{-1}$ . A plot of temporal statistics for  $\text{C}^{\text{sub}}\text{Se}^{\text{^}}$  over all 33 sample periods at all six sample locations along the Arkansas River in the downstream region is given in Fig. 4. The 85th percentile value was markedly larger than that observed in the upstream study region, increasing from 12.8  $\mu\text{g L}^{-1}$  at the most upstream station 101 to 17.6  $\mu\text{g L}^{-1}$  at station 106 downstream near the Colorado-Kansas border. By comparison, Divine and Gates (2006) reported a mean  $\text{C}^{\text{sub}}\text{Se}^{\text{^}}$  value of 2  $\mu\text{g L}^{-1}$  for samples gathered over 13 mo at the upstream end of the Lower Arkansas River, just below the outlet from Pueblo dam.

The mean value of  $\text{C}^{\text{sub}}\text{Se}^{\text{^}}$  in routine groundwater samples in the two regions was three to eight times greater than the mean value for samples from the Arkansas River. Data on quantities of infiltrated irrigation water (the bulk of which is diverted from the river), effective precipitation, and evapotranspiration reported in Gates et al. (2006) indicate that evaporative concentration causes solute concentrations in groundwater to increase by a factor of about 2 to 4 within the Arkansas River Valley. The fact that the ratio of groundwater to surface water  $\text{C}^{\text{sub}}\text{Se}^{\text{^}}$  is larger than 2 to 4, points to substantial dissolution of Se from subsurface geology and soils, especially in the upstream region.

Sampled waters in both regions were relatively saline, and while TDS was about 22% greater in groundwater samples taken downstream compared to upstream, in river water samples TDS was about 327% higher. Upstream the mean river water TDS was about 19% of the average groundwater TDS, while downstream the mean river water concentration was about 68% of that measured in groundwater. Whereas mean TDS concentration measured in tributary and drains was almost double that measured in the river in the upstream region, the two means were very similar in the downstream region. Since tributary and drain flow is dominated by groundwater return flow, this result is consistent with the finding that river water TDS more closely approaches groundwater TDS downstream along the river. The predominance of the  $\text{SO}_4^{\text{sub } 4^{\text{^-}}}$  anion was evident in the groundwater and surface water of both regions.

#### Correspondence of Selenium Concentrations with Geologic Formations

Figure 1 shows the occurrence and extent of various Cretaceous shale formations detected within approximately 1.5 m of the ground surface (Kenneth Watts, USGS, personal communication, October 2008) as estimated by Scott (1968), Sharps (1976), and Scott et al. (1978) from limited geologic exploration of the regions. Visual comparison of Fig. 2 with Fig. 1 reveals what appear to be "hot spots", or areas of relatively high  $\text{C}^{\text{sub}}\text{Se}^{\text{^}}$ , within or near the vicinity of identified near-surface shale in the study regions. These spatial patterns of  $\text{C}^{\text{sub}}\text{Se}^{\text{^}}$  in correspondence with identified shale formations within the alluvial valley were further explored quantitatively. First, a calibrated MODFLOW groundwater flow model of the study regions, similar to that described in Burkhalter and Gates (2005), was applied to estimate the average groundwater elevation contours and associated flow gradients over the period 1999 to 2007 upstream and 2002 to 2007 downstream. Next, the distance ( $L_s$ ) separating each sampled observation well from the edge of the closest identified shale within the alluvium was measured in the direction upstream along the principal groundwater flow gradient. Finally, the correlation of  $\text{C}^{\text{sub}}\text{Se}^{\text{^}}$  with  $\log L_s$  was computed. For the upstream region, a statistically significant (significance level,  $\alpha = 0.05$ ) value of -0.51 was computed for the Pearson correlation coefficient,  $r^{\text{sub } P^{\text{^}}}$ , (Ayyub and McCuen, 1997). Plots of  $\text{C}^{\text{sub}}\text{Se}^{\text{^}}$  vs.  $L_s$  and of  $\text{C}^{\text{sub}}\text{U}^{\text{^}}$  vs.  $L_s$ , both in the upstream region, are shown in Fig. 5 and 6, respectively. Scatter in the data is anticipated due to measurement error and spatial and temporal variability in (a) Se sources which include imported irrigation water as well as shales and soils subject to oxygenated dissolution, (b) evaporative concentration, (c)  $\text{NO}_3^{\text{sub } 3^{\text{^-}}}$  availability derived from fertilizer practices and affected by biochemically-affected transport processes, and (d) other influencing factors. Nevertheless, concentrations tend to increase as  $L_s$  decreases, supporting the hypothesis that shale deposits are a significant source of  $\text{C}^{\text{sub}}\text{Se}^{\text{^}}$  and  $\text{C}^{\text{sub}}\text{U}^{\text{^}}$  in this region. This matches

with an earlier description by Zielinski et al. (1995) of how Cretaceous marine shale and shale-derived soils in the Arkansas River Valley in Colorado yield not only U but also Se to solution. Computed values of  $r^2$  for  $C^{Se}$  with  $\log L^s$  and  $C^U$  with  $\log L^s$  for the downstream region were weak. This may be due to the fact that identified shale zones in the downstream region (Fig. 1) are much smaller and more fragmented than in the upstream region. This also may explain why the mean  $C^{Se}$  value of the upstream groundwater is 75% higher than the mean value downstream. Since the few identified shale deposits in the downstream region are relatively small, it seems likely that additional shale deposits remain unidentified and not accounted for in the calculations-another reason that computed correlations of  $C^{Se}$  and  $C^U$  with  $L^s$  are low.

#### Relationships of Selenium with Other Constituents and Redox Conditions

If a substantial portion of dissolved minerals in the alluvial aquifer are indeed derived from oxidation and dissolution of marine shales and shale-derived soils, and from re-oxidation of previously reduced constituents, then a significant relationship is expected between  $C^{Se}$ ,  $C^U$ , and salt ions which are also derived in part from these formations, in relation to redox conditions. Data were explored to investigate such relationships in groundwater and surface water samples over regional scales.

#### Correlation Among Constituents

Values of  $r^2$  were computed to describe the nature of the correlation between  $C^{Se}$ ,  $C^U$ , salt ion concentrations, and in situ field parameters for measurements in groundwater observation wells and at all surface water sampling locations in both the upstream and downstream study regions. Values of  $r^2$  were computed between a given variate X and a variate Y (designated as X-Y), between logs of the variates ( $\log X$ - $\log Y$ ), and between a variate and the log of a variate ( $\log X$ -Y and X- $\log Y$ ). Results are summarized in Table 4 for pairs involving the variables  $C^{Se}$ ,  $C^U$ ,  $C^{NO_3}$ , and  $C^{SO_4}$  in groundwater samples having moderate correlation ( $0.3 \leq |r^2| < 0.5$ ) or strong correlation ( $|r^2| \geq 0.5$ ) (Cohen, 1988). All correlations reported in Table 4 were statistically significant ( $\alpha = 0.05$ ) with  $p < 0.05$ . Our data reveal significant moderate relationships between  $C^{Se}$  and salinity, as expressed in terms of EC and TDS. A significant value of  $r^2$  was 0.41 for groundwater  $C^{Se}$  with EC and was 0.39 for groundwater  $C^{Se}$  with  $\log TDS$ , respectively, in the upstream study region, and were 0.49 and 0.51, respectively, in the downstream study region.

Deverel and Millard (1988) studied solutes in the shallow groundwater (water table depth  $< 10$  m) of the irrigated western San Joaquin Valley in California and concluded that the hydrologic processes that had contributed to high salinity concentrations in groundwater had also resulted in high  $C^{Se}$ . They computed correlation between  $\log C^{Se}$  and  $\log EC$  in single samples taken from 68 wells in an alluvial-fan geologic zone and in single samples from 50 wells in a basin-trough geologic zone. Computed values were significant ( $\alpha = 0.05$ ) at 0.79 and 0.44, in the alluvial fan and basin trough zones, respectively.

For surface water, values of  $r^2$  were 0.87 and 0.84 for  $C^{Se}$  with EC and with TDS, respectively, in the upstream study region. Values for the downstream study region were 0.51 and 0.56 for  $C^{Se}$  with EC and with TDS, respectively.

The computed significant value of  $r^2$  between  $\log C^{Se}$  and  $\log C^U$  for the upstream groundwater data was 0.51. For the downstream data, correlation was stronger between  $C^{Se}$  and  $C^U$  with  $r^2 = 0.70$ . Since both U and Se have been detected in Cretaceous formations like those found in the LARV (Zielinski et al., 1995; Kulp and Pratt, 2004), this moderate to strong correlation was not surprising; it further suggests that the two minerals are being dissolved and mobilized from similar geologic sources.

Zielinski et al. (1995) reported a correlation coefficient (presumably Pearson) of 0.79 between  $C^{Se}$  and  $C^U$  for 35 surface water samples gathered from the Arkansas River and its tributaries from Canyon City to near the Colorado-Kansas border. Our data show significant correlation between  $C^{Se}$  and  $C^U$  for surface water in the upstream and downstream study regions of 0.89 and 0.82, respectively.

## Redox Processes and Controls on Groundwater Constituents

The presence of redox-sensitive species such as DO,  $\text{NO}_3^-$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Mn(IV)}$ ,  $\text{Fe(III)}$ ,  $\text{U(VI)}$ , and  $\text{SO}_4^{2-}$ , depend on the succession of terminal electron-accepting processes illustrated in Fig. 7. The importance of the succession of the processes involving these species, as well as additional species often present in aquifer systems, is given by Korom (1992) and McMahon and Chapelle (2008), and is only lightly touched on here. The reduction of DO provides the highest quantity of energy for the bacteria (McMahon and Chapelle, 2008), and thus is the principal electron acceptor for bacterial respiration processes, followed by  $\text{NO}_3^-$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Mn(IV)}$ ,  $\text{Fe(III)}$ ,  $\text{U(VI)}$ , and finally  $\text{SO}_4^{2-}$ . Due to this preferential consumption of species, each constituent acts as an inhibitor of the reduction reactions with a lower redox potential. For example, investigators (Weres et al., 1990; White et al., 1991) observed, under limited localized conditions, the inhibition of  $\text{SeO}_4^{2-}$  reduction in the presence of  $\text{NO}_3^-$ , and the immediate reduction of  $\text{SeO}_4^{2-}$  on depletion of  $\text{NO}_3^-$ . Similarly, in an oxygenated environment wherein  $\text{NO}_3^-$  and  $\text{SeO}_4^{2-}$  have high concentrations, reactions involving the reduction of U and  $\text{SO}_4^{2-}$  would not occur. Field data indeed show very high  $r^2$  of 0.88 and 0.80 between  $\text{CSO}_4^{2-}$  and  $\text{C}^{\text{U}}$  in the upstream and downstream regions, respectively.

Significant power relationships between  $\text{C}^{\text{Se}}$  and  $\text{C}^{\text{NO}_3^-}$  in groundwater are illustrated in Fig. 8 and 9, suggesting the key role that  $\text{NO}_3^-$  plays in oxidation and inhibited reduction of Se in this subsurface environment. As expected, there is considerable spread in the data around the regressed trends in Fig. 8 and 9, reflecting measurement error and spatial and temporal variability in the presence of Se sources in relation to  $\text{NO}_3^-$  sources; in the nature of available electron donors; in the types of reducing bacteria; and in other influencing conditions like DO, temperature, etc.

Under conditions of thermodynamic equilibrium, ORP (and/or Eh) and pH are known to highly influence the speciation and sorption of Se (Masscheleyn, 1989, 1991), with high redox potential (200-450 mV) and high pH (7-9) resulting in high Se-solubility. Researchers have noted, however, that under field conditions, where multiple kinetic reactions are occurring, in situ measurements of ORP (using a platinum electrode) and of pH are of limited value in assessing even the overall redox status of natural waters much less the status of specific redox couples like  $\text{NO}_3^-$ - $\text{SeO}_4^{2-}$  (Runnells and Lindberg, 1990; Chapelle et al., 1996; Schuring et al., 2000). These observations were borne out in our data. Mean measured ORP values (Tables 1-3) indicated generally oxidizing conditions in both the groundwater and surface water of the LARV. However, Pearson correlation of ORP with  $\text{C}^{\text{Se}}$ , though significant, was weak to moderate at 0.27 and -0.42 for groundwater and surface water, respectively, in the upstream region and at 0.29 and 0.12 for groundwater and surface water in the downstream region. Measured pH values were found to be weakly inversely correlated with  $\text{C}^{\text{Se}}$ , having Pearson correlation of -0.15 for groundwater in the upstream region (correlation for surface water upstream was insignificant) and -0.23 and 0.16 for groundwater and surface water in the downstream region. Surface water samples from the upstream study region also revealed significant correlation between  $\log \text{C}^{\text{Se}}$  and  $\text{C}^{\text{NO}_3^-}$ , with  $r^2 = 0.37$ ; however, the number of available samples is still quite limited to date. For the much larger set of surface water samples from the downstream study region the computed value of  $r^2$  was 0.72 between  $\log \text{C}^{\text{Se}}$  and  $\log \text{C}^{\text{NO}_3^-}$ .

This strong correlation between  $\text{C}^{\text{Se}}$  and  $\text{C}^{\text{NO}_3^-}$  suggests important directions for the management of Se in rivers and reservoirs. A study by Zielinski et al. (1997) of isotopic measurements of N in surface waters of the Sixmile Creek drainage to the Arkansas River, a few miles downstream of Pueblo, revealed that  $\text{NO}_3^-$  originates from fertilizer and soil organic N in this area which is similar to the regions of the current study. Since  $\text{NO}_3^-$  is one of the primary sources of oxygen for the mobilization and retention of dissolved Se, better control of N fertilizer may be used to diminish Se loading to ground and surface water in the stream-aquifer system.

Though large, the number of observations is yet too limited for a full multivariate analysis among measured

variables. However, some multivariate relationships between  $C^{sub} Se^{\wedge}$  and other constituents were preliminarily explored using knowledge of constituent chemistry. Redox processes suggest that the inverse relationships of  $C^{sub} Se^{\wedge}$  and  $C^{sub} U^{\wedge}$  with  $L^{sub} s^{\wedge}$  should grow stronger when excluding samples having both low  $C^{sub} NO^{sub} 3^{\wedge}$  and DO values. The reason behind this phenomenon is the existence of a threshold constituent concentration at which bacteria commence to reduce the next constituent in line on the redox ladder. Frind et al. (1990), for instance, in a numerical modeling study involving the reduction of  $NO^{sub} 3^{\wedge}$  and  $SO^{sub} 4^{\wedge}$  in a groundwater system, based the model on observations that  $SO^{sub} 4^{\wedge}$  begins to be reduced once  $NO^{sub} 3^{\wedge}$  falls below a threshold concentration of  $1 \text{ mg } L^{sup} -1^{\wedge}$ . Similarly, Oremland et al. (1990) concluded that a lower threshold value of  $NO^{sub} 3^{\wedge}$  concentration exists at which both  $NO^{sub} 3^{\wedge}$  and  $SeO^{sub} 4^{\wedge}$  reduction can occur simultaneously, although a value for the threshold concentration was not provided. A similar threshold occurrence is found to be the case in the current study, with the value of  $r^{sub} P^{\wedge}$  for  $C^{sub} Se^{\wedge}$  with  $\log L^{sub} s^{\wedge}$  in the upstream region changing from -0.51 to -0.60 and the value of  $r^{sub} P^{\wedge}$  for  $C^{sub} U^{\wedge}$  with  $\log L^{sub} s^{\wedge}$  changing from -0.63 to -0.75 when including only those samples with  $C^{sub} NO^{sub} 3^{\wedge} > 10 \text{ mg } L^{sup} -1^{\wedge}$  or  $DO > 7 \text{ mg } L^{sup} -1^{\wedge}$ . This improved correlation may be due not only to the inhibition of the reduction of existing  $C^{sub} Se^{\wedge}$  but also to increased production of  $C^{sub} Se^{\wedge}$  by oxidation of seleno-pyrite from shale. These threshold values will be updated as more data becomes available, and will be valuable in modeling studies involving  $NO^{sub} 3^{\wedge}$  and  $SeO^{sub} 4^{\wedge}$ .

The schematic presented in Fig. 7, though useful, is yet simplified, and often more complex processes and relationships occur between the constituents. Suzuki and Suko (2006), for example, noted that the complexities of reactions involving the oxidation states of U are only beginning to be revealed. In other instances, bacteria may only be able to reduce a certain constituent, and thus  $SO^{sub} 4^{\wedge}$ -reducing bacteria may be inefficient at reducing U (Yabusaki et al., 2007), or there may exist species of  $SeO^{sub} 4^{\wedge}$ -reducing bacteria that do not reduce  $NO^{sub} 3^{\wedge}$  (Oremland et al., 1990).

#### Conclusions and Implications

Past data, credible yet limited, led the CDPHE to designate all reaches of the Lower Arkansas River as impaired with regard to Se contamination. A broad regional field study set out to better clarify the severity and variability of the problem; to glean information about influencing factors; and to begin building a database to guide and support future corrective action. Such action would include the adoption of BMPs to control nonpoint source loads of Se to the stream-aquifer system and, if necessary, to establish and administer TMDL<sup>sub</sup> s<sup>^</sup> to stream reaches. This paper reports on a number of important discoveries that have been made in this field study to date:

- \* Average measured  $C^{sub} Se^{\wedge}$  in the Arkansas River exceeds the current CDPHE chronic standard for aquatic habitat, not marginally but substantially-on average by a factor of 2 in the upstream and by a factor of 2 to 4 along the downstream study region;
- \* Average measured  $C^{sub} Se^{\wedge}$  in the groundwater substantially exceeds the current standard for livestock watering in both the upstream and downstream study regions and constitutes a substantially elevated concentration that is carried to streams in nonpoint source return flows;
- \*  $C^{sub} Se^{\wedge}$  in both groundwater and surface water display sizeable spatial and temporal variability, highlighting the need to account for such patterns when developing management solutions;
- \*  $C^{sub} Se^{\wedge}$  typically display moderate correlation with salinity, as indicated by TDS and EC, in both groundwater and surface water;
- \* The nature and degree of dissolution and mobilization of Se from shale and shale-derived residuum is clarified through several pieces of evidence:
- \* In the upstream region where extensive nearsurface shale formations have been identified,  $C^{sub} Se^{\wedge}$  in groundwater is found to be strongly correlated with up-gradient distance to identified shale (Ls),
- \*  $C^{sub} Se^{\wedge}$  shows high correlation and significant regression relationships with  $C^{sub} U^{\wedge}$  which has been

previously established as sourced from Cretaceous shale formations in the river valley, and

- \* The ratio of  $C^{sub} Se^{\wedge}$  in groundwater to that diverted for irrigation from the river is larger than what would be expected due to evaporative concentration alone, especially upstream;

- \*  $C^{sub} Se^{\wedge}$  tends to be related strongly to  $C^{sub} NO^{sub} 3^{\wedge}$  in groundwater, revealing in an extensive field setting the influence that  $NO^{sub} 3^{\wedge}$ , sourced and transported by fertilization and irrigation, promotes the dissolution of Se from geologic and soil material and its consequent retention in solution; and

- \* Preliminary findings on the influence of  $C^{sub} NO^{sub} 3^{\wedge}$  and DO on the correlation of  $C^{sub} Se^{\wedge}$  and  $C^{sub} U^{\wedge}$  with  $L_s$ , provide field evidence suggesting tentative threshold concentration levels of roughly  $10\text{ mg L}^{sup} - 1^{\wedge}$  for  $C^{sub} NO^{sub} 3^{\wedge}$  and  $7\text{ mg L}^{sup} - 1^{\wedge}$  for DO that inhibit reduction and promote oxidative dissolution from shale deposits. These values will be updated with the acquirement of more data.

These findings provide quantitative evidence of a serious Se problem in the Arkansas River Valley. In particular, they highlight the substantial role that dissolution processes associated with oxygenated irrigation return flows play in the contamination of the stream-aquifer system. They reveal the importance of the interplay between shale and shale-derived formations and redox reactions in understanding and predicting regional and temporal patterns of dissolved Se concentration. Moreover, they suggest some good prospects for decreasing concentrations and loads, ushering the research effort into a modeling and search-for-solutions phase.

The developed regional-scale regression relationships between  $C^{sub} Se^{\wedge}$  and  $C^{sub} NO^{sub} 3^{\wedge}$  (Fig. 8 and 9), though still in need of refinement, provide a notion of the degree to which  $C^{sub} NO^{sub} 3^{\wedge}$  must be decreased in groundwater to effect a targeted average decline in  $C^{sub} Se^{\wedge}$  over the regions, thereby contributing to a related decline in Se loads to streams. For example, to achieve 20 and 40% decreases in average  $C^{sub} Se^{\wedge}$  in the groundwater of the upstream region would require decreases of about 29 and 49%, respectively, in average  $C^{sub} NO^{sub} 3^{\wedge}$  over the region. Decreases of about 37 and 75% in average  $C^{sub} NO^{sub} 3^{\wedge}$  would be needed to achieve similar  $C^{sub} Se^{\wedge}$ -lowering targets over the groundwater of the downstream region. Planning and implementing BMPs and TMDL<sup>s</sup> to achieve successful and economical decreases in concentrations over such broad regions will require that attention be given to how flow, redox reactions, adsorption and desorption, and other processes interact to result in the most effective spatial and temporal patterns. Lowering overall Se loads from groundwater to streams will then require consideration of measures that diminish not only  $C^{sub} Se^{\wedge}$  but also rates of groundwater return flow.

The reported results are being used as a database for developing and calibrating a groundwater Se transport model of the study regions to use in evaluating improvement alternatives. Such alternatives will include interventions to decrease recharge to groundwater and the associated gradients and return flows that dissolve and carry Se to the stream system (Burkhalter and Gates, 2006) and measures to better manage N fertilizer application to lessen  $NO^{sub} 3^{\wedge}$  leaching to the shallow groundwater. Data collection in the two study regions is being refined and extended to provide enhanced understanding and broader model support.

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abstract={Prudent interventions for reducing selenium (Se) in groundwater and streams within an irrigated river valley must be guided by a sound understanding of current field conditions. An emerging picture of the nature of Se contamination within the Lower Arkansas River Valley in Colorado is provided by data from a large number of groundwater and surface water sampling locations within two study regions along the river. Measurements show that dissolved Se concentrations in the river are about double the current Colorado Department of Public Health and Environment (CDPHE) chronic standard of  $4.6 \mu\text{g L}^{-1}$  for aquatic habitat in the upstream region and exceed the standard by a factor of 2 to 4 in the downstream region. Groundwater concentrations average about  $57.7 \mu\text{g L}^{-1}$  upstream and  $33.0 \mu\text{g L}^{-1}$  downstream, indicating a large subsurface source for irrigation-induced dissolution and mobilization of Se loads to the river and its tributaries. Inverse correlation was found between Se concentration and the distance to the closest identified shale in the direction upstream along the principal groundwater flow gradient. The data also exhibited, among other relationships, a moderate to strong correlation between dissolved Se and total dissolved solids in groundwater and surface water, a strong correlation with uranium in groundwater, and power relationships with nitrate in groundwater. The relationship to nitrate, derived primarily from N fertilizers, reveals the degree to which dissolved Se depends on oxidation and inhibited reduction due to denitrification and suggests that there are prospects for reducing dissolved Se through nitrate control. Current and future results from these ongoing studies will help provide a foundation for modeling and for the discovery of best management practices (BMPs) in irrigated agriculture that can diminish Se contamination. PUBLICATION ABSTRACT}},  
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